Transitioning Submersible Chemical Analyzer Technologies for Sustained, Autonomous Observations from Profiling Moorings, Gliders and other AUVs

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LONG-TERM GOALS

To transition existing prototype autonomous profiling nutrient analyzers into commercial products that can be readily deployed on autonomous profiling moorings, coastal gliders and propeller driven unmanned underwater vehicles and used for sustained, autonomous ocean observations of chemical distributions and variability. A series of issues have been identified that that need to be addressed to convert prototype nutrient analyzers into commercial units that can be widely used by the community for sustained and accurate, stable, autonomous operation in the ocean. These issues are; (1) a more compact size, (2) reduced reagent and power consumption, (3) enhanced biofouling suppression, (4) ease of use by non-chemists, and (5) documented performance when deployed on different platforms.

Our plan to address those issues involves using recent advances in micro-fluidics and optical detectors (new SubChem and WET Labs technologies) to reduce sample flow rates and volumes and thus reagent and power consumption; (2) extend the length of field deployments by periodically isolating sensitive components so that back-flushing and chemical techniques can be used to suppress bio-fouling, (3) increase the ease of use by simplifying operation, pre-packaging reagents and outputting the data in engineering units, and (4) thoroughly documenting the performance by conducting demonstration experiments at field sites that have strong vertical and horizontal nutrient gradients and episodic phytoplankton blooms.

We are achieving these goals through this NOPP partnership. The industry partners have taken the lead in developing the commercial versions of the nutrient analyzers while the university and government partners are providing guidance defining the initial performance criteria for the nutrient analyzers and in providing the deployment platforms and conducting the field testing and demonstration experiments.

OBJECTIVES

The primary objectives of this collaborative NOPP project are the technological advancement, verification, demonstration and commercialization of two autonomous profiling nutrient analyzers that have been developed to their present status with government and private funding. The Autonomous Profiling Nutrient Analyzer **(**APNA) and the Micro-AUV Ready Chemical Analyzer (MARCHEM) will be improved so that they are capable of deployment from profiling moorings, coastal gliders and other AUVs for sustained, autonomous ocean observations of nutrient concentrations, spatial distributions and temporal variability.

APPROACH AND WORKPLAN

Our general approach to achieve these objectives involves a collaborative partnership between industry (Alfred Hanson, SubChem Systems, Inc., and Casey Moore, WET Labs, Inc.), university (Percy Donaghay, University of Rhode Island) and government (Richard Arrieta & Brian Granger, SPAWAR Systems Center - San Diego). An existing APNA prototype is being modified by SubChem Systems and WET Labs to be a more compact, resource-efficient, autonomous profiling multi-nutrient analyzer (now referred to as APNA II and III), particularly suited for sustained deployments on autonomous moored profiling systems like the IOPC profiler, and other AUVs. The MARCHEM analyzer prototype will be similarly developed, but as a very compact single channel analyzer designed for ready deployment on autonomous underwater vehicles that have more stringent space and power limitations (i.e. coastal gliders and small UUVs). Both of these analyzers will utilize similar

miniaturized electro fluidic, optical detection and instrument communication and control components to accomplish the autonomous chemical analysis with minimal utilization of power and reagents. The academic and government partners, URI-GSO and SPAWAR-SSC, will contribute to the further development of these nutrient analyzers by providing advice and guidance on the analyzer design and specifications for the purpose of integration onto specific oceanographic platforms and accomplishing specific scientific and ocean observation goals. As they are developed, the MARCHEM and APNA analyzers will be tested and demonstrated in the field by integrating and deploying them on various autonomous underwater vehicle test platforms, such as the ORCAS IOPC profiler (URI), REMUS AUV, and Slocum coastal gliders (SPAWAR-SSC).

WORK COMPLETED

Progress was made on multiple objectives during the third fiscal year of NOPP funding.

Development was completed of automated software for rapid processing of large data sets comprised of multiple profiles with APNA nutrient data. A custom MATLAB toolbox has been developed by SubChem Systems and is being applied to calculate and plot the analytical results from multiple profiles that were collected during the two-week field deployment of APNA II on the ORCAS IOPC Profiler in Monterey Bay during 2006.

Develop the capability for real-time environmental data products. The NOPP project partners have also successfully collaborated with Applied Science Associates (ASA) to develop and demonstrate the technology to autonomously acquire and communicate real-time environmental data from the ORCAS profilers, gliders, and AUVs, and to seamlessly interface this data collection system with COASTMAP^{TM} to generate useful real-time data products. COASTMAP is ASA's web-based integrated undersea data collection, management, and visualization system. This integration effort was also partially funded by the Rhode Island Science Technology Advisory Council and by the URI-NUWC Center of Excellence in Undersea Technology (COEUT).

Testing of APNA capabilities on cabled-moorings in collaboration with researchers at the University of Hawaii and the Woods Hole Oceanographic Institute. A third generation prototype of the APNA series of submersible nutrient analyzer was deployed on UH's Kilo Nalu ocean observatory during August 2007 in collaboration with Drs. Eric DeCarlo and Geno Pawlak. A similar instrument is being prepared for cabled deployment later this fall on the Martha's Vineyard Coastal Observatory, in collaboration with Dr. Heidi Sosik. The APNA III is a five channel autonomous profiling nutrient analyzer (nitrate, nitrite, phosphate, silicate and ammonia) which is configurable for multi-nutrient, time-series measurements for longer-term deployments on fixed moorings (cabled or battery). The APNA III analyzers were designed and fabricated by SubChem Systems and WET Labs provided the optical detectors and detector electronics. The APNA complements a suite of observational instruments already in place that resolve waves, tides, currents and near-shore water quality in both the Waikiki – Ala Moana and Martha's Vineyard regions.

Development of ChemFIN^{TM} – Design work was continued by SubChem Systems on a new submersible chemical analyzer. ChemFIN^{TM} (Figure 2) is a small independent sensor payload, utilizing microfluidics, and is particularly designed for "low-power" underway measurements on gliders, propeller-driven AUVs and autonomous profilers. Design work and info-exchange discussions with SPAWAR and WET Labs focused on integrating the "ChemFIN" Chemical Sensor onto the Slocum

Glider and the WET Labs AMP-100 profiler. Further progress was made this fiscal year to work with SPAWAR to define an integration path and specification for a ChemFIN prototype to be hosted on the Webb Research SLOCOM Glider. A collaboration with engineering students at UMASS/Dartmouth has also been initiated to develop a wireless communication system for ChemFIN. The development of ChemFIN is nearly complete, so it will be ready for field testing on the SPAWAR's glider and WET Labs commercial profiler during early 2008.

RESULTS

The nutrient analyzer development efforts of the NOPP partners continues to be collectively focused on developing improved fluidic pumping technologies, integrated optical sensing and mixing capabilities, advancing sensor technologies, and solving integration issues for autonomous profiling platforms. The development of new fluidic and integrated fluidic-detection technologies is required for the successful adaptation of APNA, MARCHEM and ChemFIN technologies for sustained autonomous deployments on profiling moorings and gliders.

Automated Software for Processing Nutrient Data and Generating Useful Data Products: The APNA-IOPC was deployed in Monterey Bay during a field effort sponsored by the ONR directed research initiative "Layered Organization in the Coastal Ocean (LOCO)" during July 2006. The APNA II is a four channel autonomous profiling nutrient analyzer (nitrate, nitrite, phosphate, ammonia) that was designed for deployment on URI's ORCAS IOPC profiler (Figure 1). It was programmed to collect hourly nutrient profiles for a two week time period. The large data set, comprised of over two hundred vertical profiles, is being used as the initial test data for the newly developed automated software for processing large collections of APNA nutrient profiles. An initial effort was also made to integrate the output of the automated nutrient data processing software with ASA's COASTMAP software to produce useful data products (i.e. 2D and 3D time series plots).

Testing APNA's capability for long-term deployment on cabled moorings: The APNA was deployed for initial testing at the University of Hawaii's Kilo Nalu ocean observatory during mid-August 2007 as part of Eric DeCarlo's investigation of the exchange of nutrients across the sediment-water interface. The APNA's sample intake was located approximately 10 cm from the sediment-water boundary and a sample was taken every 1 every hour to measure Nitrate, Nitrite, Phosphate, Total Ammonia and Silicate concentrations. The APNA recorded all of its data internally to a flash drive. When prompted to by its operator, The APNA nutrient data was passed through the cabled connection, back to shore. The APNA was recovered after Hurricane Flossie passed to the south of the Hawaiian Island chain between August 14^{th} and 16^{th}. The nutrient data collected is presently being processed and reviewed by the UH and SubChem researchers.

Developing ChemFIN for AUVs, Gliders and Profilers: During 2006 it was decided to shift the integration path to a micro-fluidic based analyzer that would allow for a design of an externally mounted UUV/Instrumentation package called ChemFIN™ (Figure 2). A ChemFIN design review meeting, held in San Diego with partners from SPAWAR (Arrieta, Granger, et al.) in late January 2007 led to an improved specification for the best means of integrating the ChemFIN single channel analyzer on to the SPAWAR SLOCOM Glider. The NOPP partners involved determined the best interface to the SLOCOM Glider would be the wing interface to the hull. A new wing interface would be designed to allow the ChemFIN housing to be clamped to the port or starboard side along the centerline of the glider. A hydrodynamic replica of the ChemFIN housing or the ChemFIN reagent

housing itself would be fastened to the wing interface on the opposite side. This would aid in vehicle stability. Partners also determined the best electronic interface to the vehicle would be a new multi-cable termination at the aft end of the glider that would have another cable running forward to the ChemFIN housing end cap. As part of risk mitigation, SPAWAR was provided a ChemFIN software simulator for a micro-controller they had in house. This allowed for software development for the SLOCOM Glider in the absence of the ChemFIN NOx analyzer. Software Engineers from both SPAWAR and SubChem Systems were able to collaborate remotely and design a potential mission scenario and interface for the ChemFIN.

Since the design goal for the ChemFIN analyzer was to take the existing SubChem Systems technology and streamline it to a more efficient system, the major design change was to move to a micro-fluidic based system. The early 2007 calendar year was spent locating and starting dialog with vendors to layout a concept micro-fluidic manifold. SubChem Systems was able to engineer, provide specification documentation for, and have two prototype micro-fluidic manifolds fabricated. Since the April/May timeframe, emphasis was placed on trying to define and study the dynamics of the fluidic paths incorporated into the manifold. Testing with this manifold continues as technology is currently being investigated to provide more accurate flow characteristics at such low flow rates (100 microL/min). One of the biggest challenges has been to design the system with components capable of low flow rates while maintaining the capability to allow the ChemFIN payload to be subject to ocean hydrostatic pressure.

To improve the efficiency of power and chemical capability/stability, a design for a temperature control algorithm was devised incorporating multiple strategically placed temperature sensors. Experiments were performed with traditional thermocouples vs. small high precision thermistors. A new electronic and software design was completed and tested on the MARCHEM. Since signal response improved noticeably in the MARCHEM, a similar temperature control algorithm was developed for the APNA. The temperature control algorithm centers on a set temp and minimizes the amount of energy needed to maintain consistent sample flow temperature based on various temperature gradients throughout the instrument. Given the improvements seen in the MARCHEM and APNA bench testing, the temperature control algorithm will be ported to ChemFIN thin film heater control for the prototype manifold.

IMPACT/APPLICATIONS

It is a critical gap that the oceanographic community does not currently have the capability to make routine and sustained nutrient measurements, *in situ* and autonomously, at the same space and time scales that are possible for temperature, salinity, oxygen, and chlorophyll fluorescence. In recent years, though, there has been significant progress in the development and application of reagent-based optical multi-nutrient sensors. The on-going research for this NOPP project is giving us the opportunity to further develop, improve and demonstrate these autonomous chemical profiling technologies. These efforts represent substantial advancements in the development of this technology and bring us much closer to a demonstrated capability for sustained, autonomous ocean observations of nutrient distributions and variability.

TRANSITIONS

The APNA instrumentation is now commercially available from SubChem Systems, Inc and WET Labs, Inc. Two systems have been delivered, and three are presently on order, to academic research institutions for coastal research on nutrients.

The MARCHEM AUV nutrient sensing payload is slated for integration into HYDROID's REMUS-600 as part of the coastal component of the NSF Ocean Observatories Initiative. A contract is also in place with the Naval Research Laboratory (NRL) to adapt the MARCHEM AUV payload to utilize NRL immunosensor technology for the underwater detection of explosives and other chemicals of interest that may be detected by the successful NRL analytical technology.

RELATED PROJECTS

A related project is the ONR sponsored Directed Research Initiative entitled "Layered Organization in the Coastal Ocean (LOCO)". The LOCO program is focused on developing an understanding of the dynamics of thin plankton layers in coastal waters. New nutrient monitoring technologies developed in this NOPP project were demonstrated and utilized within the LOCO field research during 2005 and 2006. PIs Hanson (SubChem) and Donaghay (URI) both have LOCO projects.

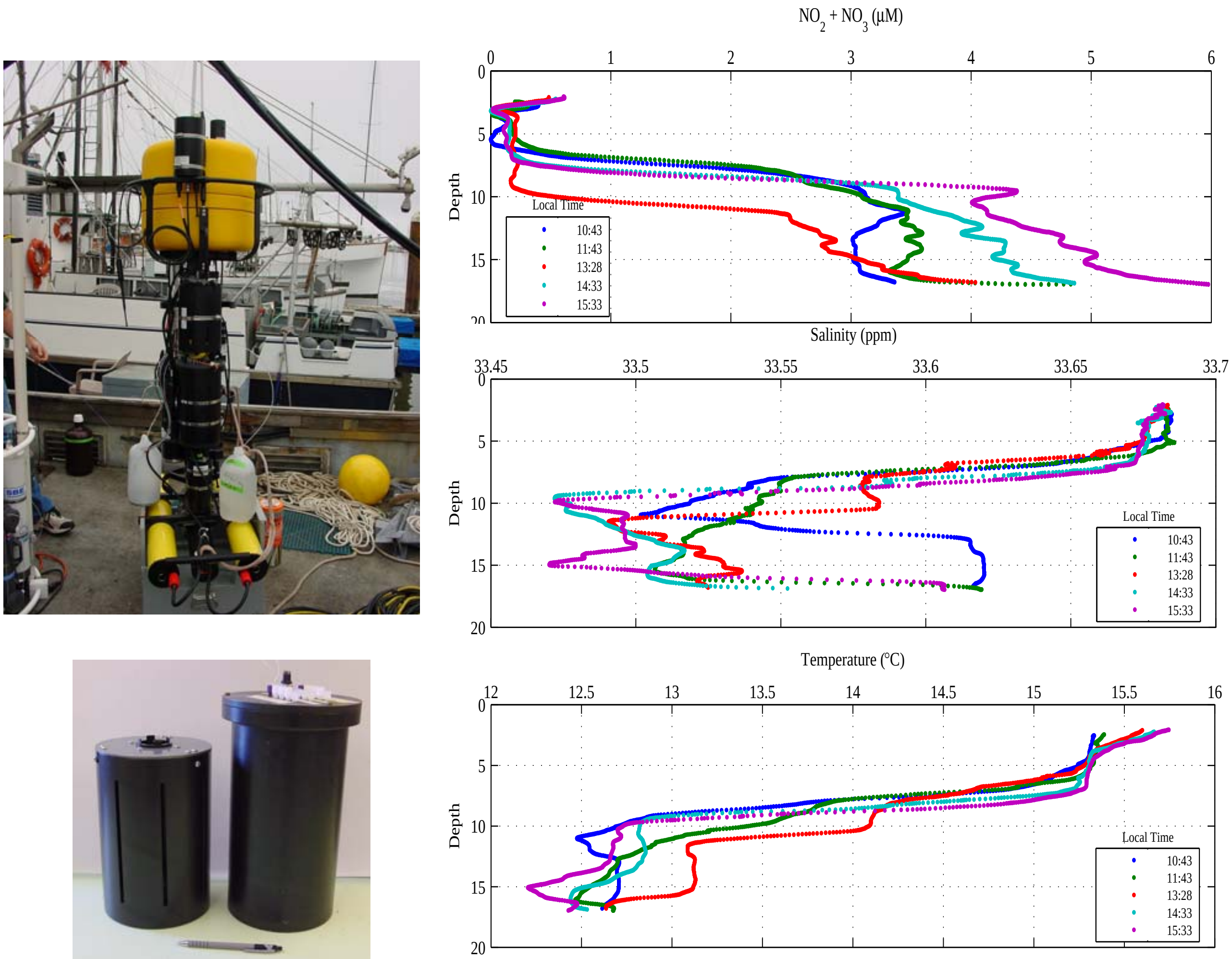

Figure 1. The IOPC profiler with the APNA II nutrient analyzer payload ready for deployment in Monterey Bay from the R/V Shana Rae and examples of hourly profiles for nitrate (top), salinity (middle), and temperature (lower) that were obtained autonomously with the system in Monterey Bay.
[The URI IOPC profiler is an autonomous, battery operated moored-profiler that may be deployed in the coastal ocean for weeks at a time. It contains a full suite of instruments and sensors for monitoring the physical, optical, biological and chemical properties of the water. The profiler can be programmed to make repeated profiles, from the bottom to the surface, on a pre-set time schedule, to send the multi-parametric results by radio telemetry to a shore- or ship-based receiver station, and then return to the bottom to wait for the time to start the next profile.]

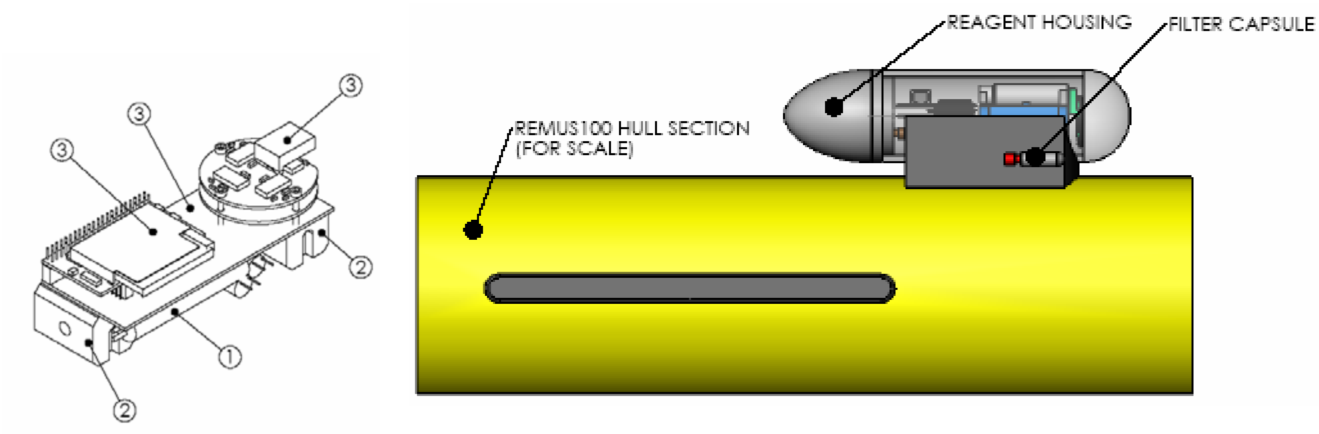

Figure 2. SubChem Systems's compact design for ChemFIN^{TM} the next generation chemical sensing payload for AUVs, Gliders and Profilers. The ChemFIN compact microfluidics(1), optical detection(2) and electronics(3) systems (left) and housing (right) externally mounted onto a REMUS vehicle hull section.
[The ChemFIN^{TM} is designed as an independent compact payload containing a micro-fluidic chemical analyzer that minimizes the power and space demands on the AUV platform.]